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Periodic Acid, a Novel Oxidant of Polycyclic, Aromatic Hydrocarbons *

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Certain polycyclic, aromatic hydrocarbons can be oxidized with periodic acid in aprotic solvents containing a small proportion of water. A unique, two-fold character of response to periodic acid by these hydrocarbons has been found: (1) production of a coupling reaction through a radical intermediate [conversion of pyrene into 1,1′-bipyrene, and fluorene into 1,2-bis(2,2′-biphenylylene)ethylene] or (2) conversion into quinones by a two-equivalent oxidation mechanism that does not involve a radical intermediate [acenaphthene, anthracene, anthrone, benz[*a*]anthracene, naphthacene, naphthalene, and phenanthrene]. Little or no reaction was observed when oxidation was attempted with sodium metaperiodate instead of periodic acid.

Electron-spin resonance revealed no radical intermediate in the oxidation of malonic acid with either periodic acid or sodium periodate.

Key Words: Aprotic solvents; aromatic hydrocarbons; malonic acid; periodic acid; pyrene radical; quinones; reaction mechanism; sodium metaperiodate.

1. Introduction

Recently in this laboratory [1],[1] the fate of certain of the polycyclic, aromatic hydrocarbons that have been identified as constituents of polluted air has been studied under conditions simulating those that these substances encounter as air pollutants; that is, (a) in the presence of ultraviolet irradiation, (b) exposure to air and slight heat, and (c) contact with powdered solids (particulates). Oxidation of many of the hydrocarbons studied occurs under such conditions. In order to identify the products, it was necessary to synthesize possible oxidation products for use as reference materials.

The main object of the present report is to describe the usefulness of periodic acid for the oxidation of polycyclic, aromatic hydrocarbons. Numerous reagents have been used to effect such oxidations, including the Milas reagent [2], the Fenton reagent [3], benzoyl peroxide [4, 5], benzyl radicals [6], phenyl radicals [7], and other free-radical reagents [8], lead tetraacetate [9, 10], ozone [11–14], and peroxy acids [15] including hydrogen peroxide in acetic acid [16], peroxyacetic acid [17, 18], and peroxytrifluoroacetic acid [19–21]. In addition, there are autooxidations [22], metabolic oxidation [23], peroxidase oxidation [24], photooxidation using solutions [25], photooxidation on solids [1], one-electron transfer oxidation [26], and various other methods [27].

Periodic acid (or its salts) has been used extensively for cleavage of 1,2-glycols, and α-hydroxy-aldehydes and -ketones [28–33]. In aprotic solvents containing some water, periodic acid has been used for the oxidative hydroxylation of an active methylene group [34–36], for oxidative cleavage of enols and reductones [37, 38], and for hydroxylation and further oxidation of compounds containing an isolated double bond, e.g., cinnamic acid [39] and cholesterol [40].

The application of periodic acid alone as an oxidant for polycyclic, aromatic hydrocarbons has not hitherto been reported [33, 41]. Sodium metaperiodate has, however, been used conjointly with such diol-forming agents as osmium tetraoxide or ruthenium tetraoxide [42]. The present study shows that, when it reacts with certain polycyclic, aromatic compounds, periodic acid has the ability to (1) produce radicals by abstraction of (a) electrons or (b) protons, (2) oxidize a methine group at an activated double bond of polycyclic, aromatic compounds, or (3) oxidize an activated methylene group.

2. Reaction Conditions

2.1. Solvent

The choice of a solvent in which to oxidize polycyclic, aromatic hydrocarbons with periodic acid appears to

*Preliminary communication: Chem. Commun. **1967**, 1087.

[1] Figures in brackets indicate the literature references at the end of this paper.

be very important. In the present work, glacial acetic acid was usually the first solvent investigated; sometimes, propionic acid could be used. In most cases, oxidations in formic acid afford lower yields than in acetic acid. A series of aprotic solvents, miscible with water and relatively stable in the presence of periodic acid at elevated temperature, was tried. These solvents, in the order of their decreasing stability to the oxidant are: *N,N*-dimethylformamide, *p*-dioxane, acetonitrile, acetone, tetrahydrofuran, methyl sulfoxide, and acetic anhydride. Methyl sulfoxide was used in the oxidation of anthracene with good results, but its application with other hydrocarbons has not yet been explored.

The stability of *N,N*-dimethylformamide in the presence of periodic acid has previously been indicated [43]. Such solvents as formamide, 2-methoxyethanol, bis(2-methoxyethyl) ether (diglyme), or 1,2-dimethoxyethane are not suitable as the reaction medium, because of instability in the presence of periodic acid at elevated temperature. When acetic anhydride was used in the oxidation of pyrene with periodic acid, with application of heat, a violent reaction occurred.

2.2. Temperature

To initiate oxidation of polycyclic, aromatic hydrocarbons with periodic acid, some degree of heating was found to be necessary. In the conversion of pyrene (**1**) into 1,1′-bipyrene (**2**) only mild warming (40 to 50 °C) was necessary; however, dimerization of fluorene (**20**) into 1,2-bis(2,2′-biphenylylene)ethylene (**24**) required a much higher temperature. The oxidations that resulted in quinone formation usually require 5 to 10 min of heating at 95 to 130 °C to start; then the temperature must be lowered to 60 to 80 °C to avoid vigorous and sometimes violent reaction. Usually, the beginning of the oxidation (and the end of the induction period) is noted by a change of the reaction medium from colorless to red or brown-red; sometimes, this is followed by evolution of iodine vapor.

2.3. Proportion of the Oxidant

Oxidative dimerization of pyrene (**1**) to 1,1′-bipyrene (**2**) was effected with a 1:1 mole ratio of periodic acid to hydrocarbon. In this reaction, it was possible to demonstrate stoichiometric consumption of the periodic acid. However, in the oxidation of the other hydrocarbons to quinones, approximately 4.2 moles of the oxidant were used per mole of hydrocarbon. This proportion was employed on the assumption that, in each hydrocarbon molecule, two methine or methylene groups become hydroxylated and then oxidized to the corresponding quinone.

2.4. Compounds Oxidized

Three kinds of polycyclic, aromatic hydrocarbons were used in the oxidations: (1) compounds having the acene structure with two active methine groups [naphthacene (**3**), anthracene (**4**), naphthalene (**7**), benz[*a*]anthracene (**12**), and pentacene (**17**)], (2) a compound having the phene structure and one active methine group [pyrene (**1**)], and (3) compounds having one or two active methylene groups [anthrone (**8**), acenaphthene (**15**), and fluorene (**20**)]. Malonic acid (**14**), which has an active methylene group, was also oxidized. In addition, the following condensed-ring, polycyclic, aromatic hydrocarbons were tested: biphenyl, chrysene, coronene, fluoranthene, perylene, picene, *p*-terphenyl, and triphenylene.

3. Results and Discussion

3.1. Effect of Solvent

The effect of various solvents on the reaction may be seen from the following examples: oxidation of phenanthrene (**10**) with periodic acid gave a poor yield (3–6%) of phenanthrenequinone (**11**) in *N,N*-dimethylformamide or in glacial acetic acid, but a good yield (45–55%) in *p*-dioxane. Anthracene (**5**) afforded a moderate yield (30%) of anthraquinone (**6**) in acetic acid, a good yield (50 to 60%) in acetone or methyl sulfoxide, and an excellent yield (90%) in *N,N*-dimethylformamide. Naphthalene (**7**) in *p*-dioxane was practically unaffected; but, in acetic acid, showed oxidation in good yield (70%) to 1,4-naphthoquinone (**9**). Naphthacene (**3**) gave a low yield (10–15%) of naphthacenequinone (**4**) when oxidized in *p*-dioxane or acetic acid, but an excellent yield (80%) in *N,N*-dimethylformamide. Pyrene (**1**) was not oxidized in *N,N*-dimethylformamide, *p*-dioxane, acetone, or ethanol, but was oxidized in acetic acid. Fluorene (**20**) was not affected in *N,N*-dimethylformamide, *p*-dioxane, or acetonitrile, but dimerized in acetic acid.

It may be concluded from these experiments that the solvent participates in the overall reaction process. As noted by Ritchie and co-workers [44], the effect of the solvent on reactions in solution is associated with a so-called solvent reorganization, and this factor may make an appreciable contribution to energies of activation in solution. Furthermore, the polarity of the solvent may partake in promotion of the rate of oxidation, by hydrogen bonding in the transition state.

3.2. General Reactivity of Polycyclic, Aromatic Compounds Toward Periodic Acid

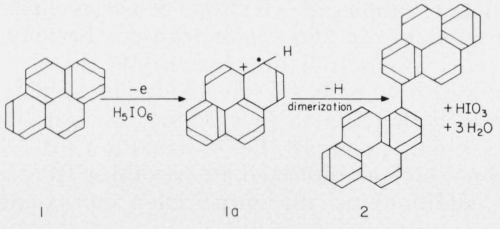
Results obtained in this study on the action of periodic acid on a variety of polycyclic, aromatic hydrocarbons reveal that linear and angular polycyclic, aromatic hydrocarbons having the acene structure (anthracene, benz[*a*]anthracene, naphthacene, pentacene, and their analogs) [45] are the most reactive; next are the condensed-ring aromatic compounds having the phene structure (acenaphthene, benzo[*a*]pyrene, pyrene, etc.) [46]; and chrysene and picene are less reactive. Little or no reaction was observed with biphenyl, coronene, fluoranthene, perylene, *p*-terphenyl, and triphenylene.

The stability of perylene and triphenylene toward periodic acid may partially be explained by an asymmetric annelation effect [47, 48], by which a hydrocarbon attains the maximum number of aromatic sextets and, consequently, the maximum degree of stability. Other factors that may influence the reactivity of polycyclic, aromatic hydrocarbons toward periodic acid are: (1) basicity of the hydrocarbon [49, 50], (2) presence of a reactive bond or a free-valence center [51, 52, 53], or a position of highest unpaired electron-densities [54, 55] or high unpaired spin-densities [56], (3) ability of periodic acid (as an electrophile) to form an association complex with a hydrocarbon, and (4) the ionization potential of the hydrocarbon [57, 58]. Increasing reactivity toward periodic acid is usually paralleled by a decreasing ionization potential of the hydrocarbon, as follows: naphthacene (**3**) > pentacene (**17**) > pyrene (**1**) > anthracene (**5**) > phenanthrene (**10**) > naphthalene (**7**). This may explain why naphthacene (**3**), having an ionization potential of 6.92 eV. [57], is most reactive, and naphthalene (**7**), having an ionization potential of 8.60 eV. [57], is the least reactive in the series.

In general, periodic acid preferably attacks a reactive center instead of a reactive bond of the aromatic ring in the polycyclic hydrocarbons. For example, anthracene (**5**) is attacked by periodic acid at the most reactive (*para*) centers (9,10-positions), instead of at the most reactive bond (the 1,2-positions). Phenanthrene (**10**) is attacked at the 9,10-positions, which constitute the most reactive bond and are the most reactive centers of the hydrocarbon.

a. Oxidation of Pyrene With Periodic Acid (1 : 1 Mole Ratio)

Treatment of pyrene (**1**) with periodic acid (1 : 1 mole ratio) in aqueous acetic acid has been shown [59] to give 1,1′-bipyrene (**2**) in a yield of over 70 percent. The formation of the radical intermediate postulated [59] in the coupling reaction has now been verified by electron-spin resonance measurement, and the pyrene radical (**1a**) has been observed at room temperature. Thus, oxidative dimerization of **1** to **2** probably proceeds through intermediate **1a** as depicted. Abstraction of a π-electron by a molecule of periodic acid from an aromatic nucleus would produce the pyrene radical **1a**; dimerization to the stable 1,1′-bipyrene (**2**) would follow the loss of one proton [60–62]. The overall oxidation process of **1** to dimer **2** involves the loss of two protons. In its ability to abstract an electron from the aromatic ring, the acceptor (periodic acid) functions like organic peroxides, which generally abstract electrons from donor molecules [63].



The mechanism of π-electron abstraction and loss of a proton involved in the dimerization of **1** to **2** resembles the mechanism recently proposed by Cooper and Waters [64, 65]; this is an outer-sphere mechanism postulated to operate in the oxidation of aromatic hydrocarbons by cobaltic ions. Acetic acid may, by solvation, protect the radicals prior to dimerization. As may be seen by examination of a model of dimer **2**, dimerization of the radical cations (**1a**) probably proceeds by their approaching each other head-to-head to give a less sterically hindered product. The e.s.r. spectrum of pyrene radical **1a** is shown in figure 1 (spectrum A).

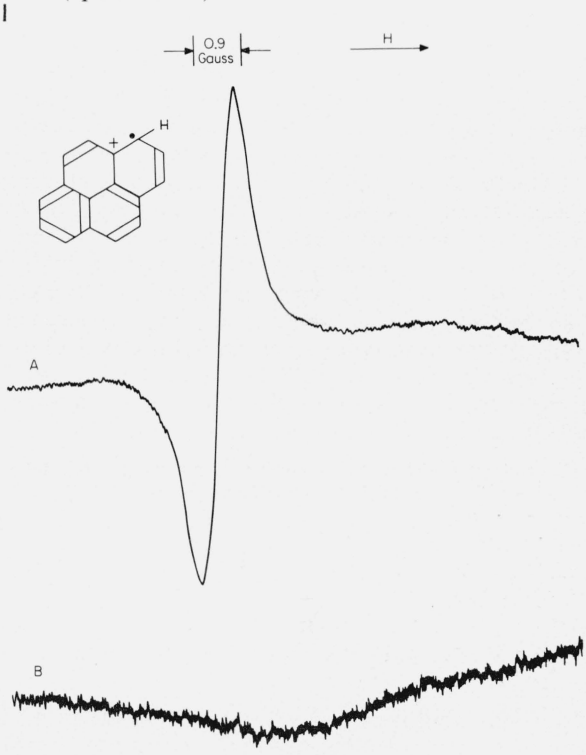


FIGURE 1. *(A) The electron-spin resonance spectrum of pyrene radical* **1a** *prepared by treatment of pyrene (in acetic acid) with periodic acid,* H_5IO_6 *(in water) at room temperature,* g = 2.0041. *(B) Anthracene (in* N,N*-dimethylformamide) on treatment with periodic acid in water. Sample B seen under comparable conditions. No radicals were observed, and the upper limit of radical concentration is at most* $^1/_{1000}$*th of that in sample A.*

The absence of the hyperfine structure for the pyrene radical cation (**1a**), as compared to the seven-line spectrum of the equivalent [54, 66] pyrene anion radical (splitting constant 1.09 gauss) [67] may be explained on the basis of a probable interaction of the π-electron radical (**1a**) originally formed with oxygen, to give a relatively stable pyrene peroxide (sigma) radical of type **24**; this reaction is probably in competition with the dimerization of **1a** to **2**. The oxygen was probably supplied by periodic acid, because dilution and deoxygenation (by bubbling nitrogen into the diluted solution) produced a similar one-line e.s.r. spectrum. It is known that dissolved oxygen can cause line-broadening in the e.s.r. spectrum by spin–spin inter-

action (dipole interaction); the spectrum can also be narrowed to one line by exchange interaction between the radical and the hydrocarbon.

b. Oxidation of Pyrene With Periodic Acid (1:4 Mole Ratio)

Treatment of pyrene (**1**) with periodic acid (1:4 molar ratio) at 95 °C initially affords green-yellow **2** which, on further stirring (30 min), changes to lustrous, brown crystals. The resulting crystalline compound is probably an addition complex between **2**, iodine, iodic acid, or periodic acid; but the structure of the compound is not yet known. The product cannot be recrystallized without loss of iodine. Analysis of the unknown indicated the presence of up to 59 percent iodine; titration of a solution of the unknown in *N,N*-dimethylformamide with sodium thiosulfate in acidic solution, and with arsenite in basic solution, confirmed the presence of iodine and iodate. The product loses iodine on being heated at 230 °C/0.05 mm, to yield crude **2** (identified by thin-layer chromatography) in addition to an unknown iodo compound. The same result was observed when the unknown was heated with a 30 percent aqueous solution of sodium hydrogen sulfite. Recrystallization of the unknown compound from boiling, glacial acetic acid gave a very small yield of the new compound as light-brown crystals; its infrared spectrum showed two bands, at 5.75 (nonconjugated C=O) and at 6.1 μm (conjugated C=O).

c. Oxidation of Polycyclic, Aromatic Hydrocarbons to Quinones; Possible Reaction Mechanisms

As reported by Bunton [68], periodic acid in aqueous solution exists as an equilibrium between the free acid and its various anions. When an aqueous solution

$$H_5IO_6 \leftrightarrows H_4IO_6^- \leftrightarrows H_3IO_6^{2-} \leftrightarrows H_2IO_6^{3-}$$

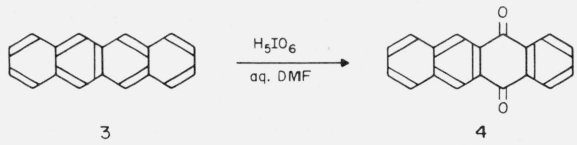
of periodic acid is mixed with an excess of acetic acid (or other water-miscible solvent used in the reaction), the equilibrium is shifted to the left (undissociated acid). Hence, under the reaction conditions described, periodic acid can function as the free acid and as the monoanion; these two forms will be used here in discussing possible reaction mechanisms for the oxidation of a variety of polycyclic, aromatic hydrocarbons to quinones.

It is assumed that, in the oxidation of polycyclic, aromatic hydrocarbons having a reactive center and a methine group, the properties of which can be compared to the nucleophilic character of the olefinic group [69], the attacking species is free periodic acid (an electrophile); whereas, in the oxidation of polycyclic, aromatic hydrocarbons having an active methylene group, which is more acidic than the methine group, the attacking species is probably the monoanion of periodic acid (a supplier of active hydroxyl groups); thus, the oxidizing species involved depends on the nature of the hydrocarbon employed.

To determine whether periodic acid would serve as a general reagent for effecting coupling reactions similar to that described for pyrene, a number of other polycyclic, aromatic hydrocarbons were treated with this reagent. Although it was found that many of these hydrocarbons are indeed affected by periodic acid, the reaction that occurs is oxidation to quinones instead of coupling.

d. Oxidation of Naphthacene (3)

A solution of naphthacene (**3**) in *N,N*-dimethylformamide was oxidized with aqueous periodic acid in a 1:4 mole ratio, to give 80 to 85 percent of naphthacenequinone (**4**). In a similar way, a series of other hydrocarbons have been converted into quinones, as described in the experimental part.



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e. Oxidation of Anthracene (5)

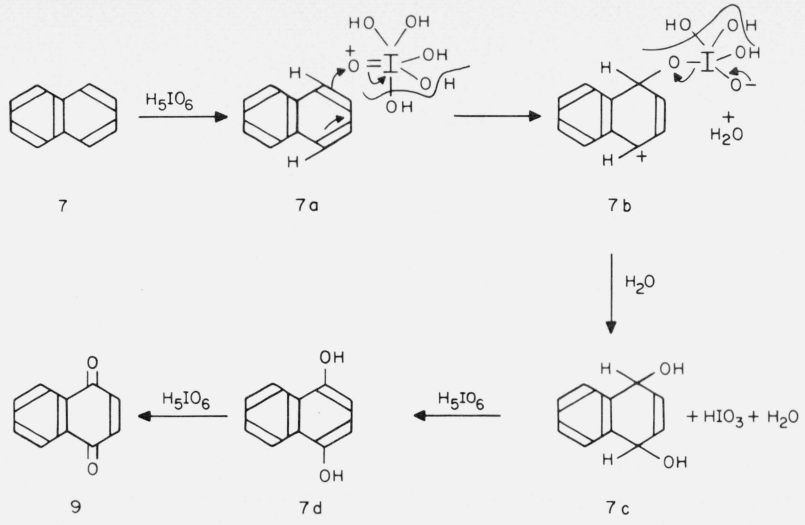
In order to determine whether these reactions with periodic acid involve a free-radical mechanism, the oxidation of anthracene (**5**) was examined in the presence of inhibitors and radical-capture agents [70, 71].

Equimolar proportions (0.01 mole) of anthracene (**5**) and (a) acrylamide, (b) methyl methacrylate, (c) acrylonitrile, or (d) 2,5-di-*tert*-amylhydroquinone were stirred at 75 °C with periodic acid (0.04 mole) in 25:4 (v/v) acetonitrile—water (145 ml) for 45 min; in each case, a high yield of anthraquinone (**6**) was obtained, and practically no polymerization of reagents *a*, *b*, or *c* was observed. In the experiment with *d*, some yellow 2,5-di-*tert*-amylbenzoquinone crystallized out when the filtrate was cooled. Thus, these experiments gave no evidence of radical participation in the oxidation of **5** to **6**, a conclusion confirmed by e.s.r. monitoring of the oxidation path in the range from 0 to 100 °C in aqueous *N,N*-dimethylformamide or aqueous acetic acid. As may be seen from figure 1, the e.s.r. spectrum B for oxidation of **5** shows no radical; whereas, the dimerization of **1**, as discussed earlier, proceeds through a radical intermediate (spectrum A).

f. Oxidation of Naphthalene (7); Mechanism for Oxidation of an Active Center and a Methine Group

As suggested in the previous communication [59], the first step in the mechanism of the oxidation of naphthalene may involve association between periodic acid (an electrophile) and the free-valence center of the aromatic ring [51–53], or with a position having the highest unpaired electron densities [54]; these possibilities are in agreement with the basicity of the polycyclic, aromatic hydrocarbons [49, 50].

The reaction path for the oxidation of polycyclic, aromatic hydrocarbons to quinones by periodic acid may be contrasted with that of oxidation with chromic acid, for which an intermediate (resulting from electrophilic addition) as the initial step in oxidation of



alkenes and polycyclic, aromatic hydrocarbons has been postulated [78, 79]. For example, the mechanism for the oxidation of naphthalene (**7**) to 1,4-naphthoquinone (**9**) apparently proceeds by a two-equivalent oxidation. This reaction involves electrophilic attack of periodic acid, as shown in **7a**, with the formation of intermediate **7b**. Collapse of **7b** by loss of iodic acid, and addition of water to the cationic center of **7b**, affords the 1,4-dihydro-1,4-diol (**7c**), which is then rapidly oxidized by periodic acid to dione **9** in 70 percent yield. The transformation of **7b** to **7c** is supported by the fact that only the mononegatively charged ion of periodic acid decomposes, and that the undissociated or dinegatively charged intermediate is inert to oxidative decomposition [80, 81, 82, 83]. The last step in this sequence of reactions is supported by the observation that 1,4-naphthalenediol (**7d**) is oxidized with periodic acid to dione **9** in a yield of 80 percent.

The suggested mechanism for the oxidation of **7** to **9** is another possible way in which periodic acid can transfer its oxygen atom to an aromatic moiety. Hence, the behavior of periodic acid toward polycyclic, aromatic hydrocarbons has a unique, two-fold character; it can (1) produce coupling products through a radical intermediate, or (2) convert them into quinones, apparently by a two-equivalent oxidation mechanism that does not involve a radical intermediate.

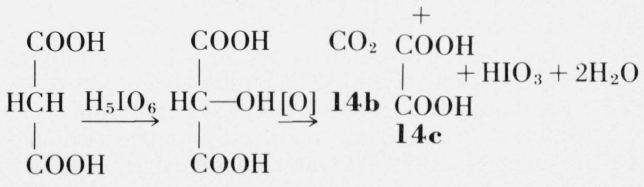
g. Oxidation of Anthrone (8); Mechanisms for the Oxidation of an Active Methylene Group

The oxidation of anthrone (**8**) with periodic acid was also investigated. This compound has a benzilic type of methylene group, similar to the methylene group of tetralin (**19**), for which a chain-radical intermediate, analogous to **8a** and supposedly initiated by treatment of **19** with chromic acid or periodic acid, has been postulated [72]. However, e.s.r. monitoring of the reaction mixture obtained on treatment of anthrone (**8**) with periodic acid showed no radicals, thus excluding scheme B, which would proceed through a radical intermediate (**8a**). Similar autoxidation of tetralin (**19**) to the hydroperoxide, which may involve a chain-radical intermediate, has been reported [72, 73].

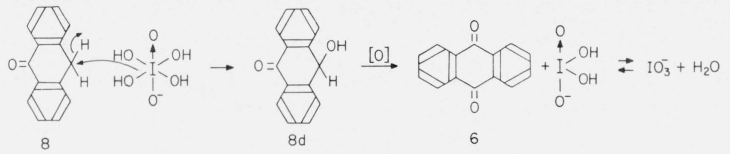
It is believed that oxidation of anthrone (**8**) to anthraquinone (**6**) proceeds by a push-pull mechanism, as depicted in scheme A; a monoanion of periodic acid functions here as an active hydroxylating species; the dihydro intermediate **8d** is probably then oxidized further to anthraquinone (**6**). The attack by a monoanion of periodic acid on a methylene group of **8** is a type of insertion of a ligand oxygen atom into a C—H bond; this may possibly be the way in which the active oxygen of periodic acid is transferred; an alternative way, postulating the insertion of an unbound oxygen atom, was suggested by Bunton [74]. The insertion mechanism in the ozone oxidation of fluorene or anthrone has recently been proposed [14].

3.3. Oxidation of Malonic Acid (14)

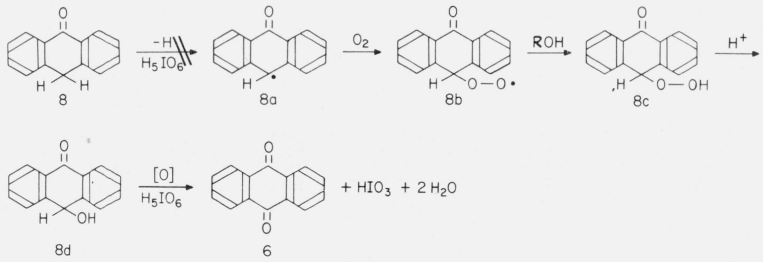
Oxidation of malonic acid (**14**) with periodic acid or sodium periodate has been thoroughly studied [35, 75], and the products **14b** and **14c**, which may arise from intermediate **14a**, have been isolated and



identified [35, 75]. Assuming that products **14b** and **14c** arise from **14**, as reported [35, 75], this oxidative cleavage reaction has been checked for possible participation of free radicals. By means of e.s.r. measurements, hydroxylation of malonic acid (**14**) with periodic acid and sodium periodate was examined in water; monitoring of the reaction path (at 0 to 60 °C) did not reveal free radicals, in agreement with an earlier ob-



SCHEME A



SCHEME B

servation [36] obtained by chemical evidence (no polymerization of acrylonitrile).

It is also believed that the reported [35, 75] hydroxylation of an active methylene group in malonic acid (**14**) and its derivatives by periodic acid or sodium periodate in aqueous solution also proceeds by a ligand push-pull mechanism, similar to that described for anthrone (**8**) (see sec. 3.8), although direct transfer of an oxygen atom by periodate to the active methylene group of malonic acid (electrophilic oxidation) has also been proposed [74]. However, x-ray irradiation of crystals of malonic acid (**14**) produces radicals having an unpaired electron centered on a methylene carbon atom [76, 77].

Finally, hydroxylation of an active methylene group of an acyclic compound (such as malonic acid and its derivatives) can be effected by periodic acid and sodium periodate, whereas the hydroxylation (and oxidation) of an active methylene group in polycyclic, aromatic hydrocarbons can be effected only by periodic acid, and no oxidation has been observed with sodium periodate.

3.4. Oxidative Coupling of Fluorene (20); Mechanism of Oxidation of an Extremely Active Methylene Group

Fluorene (**20**) has an unusually active methylene group [84], and consequently, it is an extremely reactive hydrocarbon. Treatment with periodic acid (1:2 mole ratio) in warm aqueous acetic acid produced a coupling product, 1,2-bis(2,2′-biphenylylene)ethylene (**23**), in about 10 percent yield. E.s.r. monitoring of the oxidation reaction at room temperature revealed the presence of a radical (moderate intensity), as shown in figure 2. A plausible reaction mechanism that can explain the formation of the coupling product (**23**) is shown here; periodic acid anion abstracts a hydrogen atom from a methylene group in **20** with formation of a radical (**21**); dimerization of **21** gives hydrocarbon **22**; elimination of two protons produces the orange-red **23**. Only traces of fluoren-9-one (**26**) could be identified in the reaction mixture (thin-layer chromatography); this mixture was not analyzed for its fluorene hydroperoxide (**25**) content. The low yield

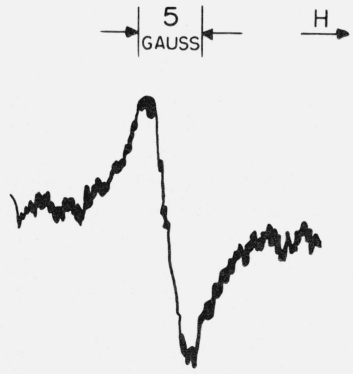


FIGURE 2. *The e.s.r. spectrum of fluorene radical, prepared by treatment of fluorene (in acetic acid) with periodic acid, H_5IO_6 (in water) at room temperature,* $g = 2.0036 \pm 0.0002$.

of hydrocarbon **23** can be explained on the basis of the relative reactivity of radical **21**, which apparently quickly absorbs oxygen (either from the air, or from the oxidant) to give the stable fluorene radical (**24**).

This is then easily converted into the stable fluorene hydroperoxide (**25**). Thus, the radical **21** may alternatively interact with oxygen prior to dimerization; fluorene (**20**), as known, reacts with molecular oxygen to give a stable hydroperoxide (**25**). Moreover, a possible interaction of radicals **21** and **24** can also contribute to lowering of the yield of the product. The above reaction is, therefore, a second example we have found of oxidative dimerization which proceeds through a radical intermediate.

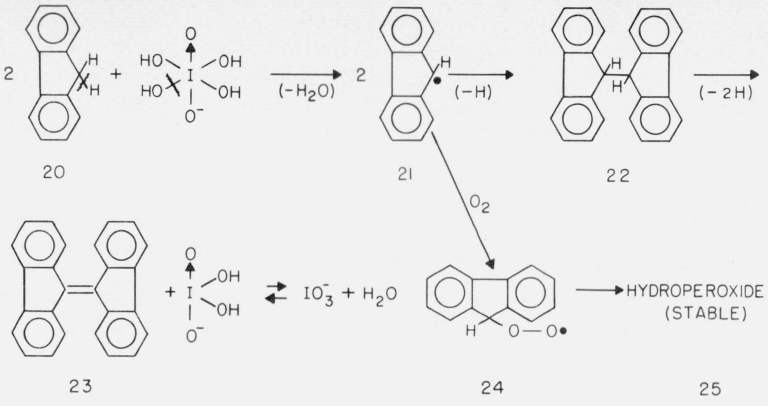
Radical **21** has probably lost its hyperfine structure on contact with oxygen, and the hydroperoxide radical **24** is probably responsible for the broad, one-line e.s.r. spectrum that is actually observed (see fig. 2).

4. Experimental Procedures

4.1. Spectral Measurements

Infrared absorption spectra of compounds were recorded with Perkin-Elmer Model 137 and Model 257 spectrophotometers.[2] E.s.r. spectra were recorded

[2] Certain commercial instruments are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.



with a Varian Model 4500 EPR Spectrometer with 100-kHz field modulation; the samples were placed in a Varian Model V–4548 aqueous-solution sample-cell.

4.2. Purification of Quinones

Final purification of crude quinones was performed by column chromatography (silica gel, 100–200 mesh, acetic acid or benzene–acetic acid as eluant), by a technique described elsewhere [85].

4.3. Treatment of Pyrene (1) With Periodic Acid (1:1 Mole Ratio)

Treatment of pyrene (**1**) (0.1 mole in acetic acid) with periodic acid (0.1 mole in water) yielded a coupling product, 1,1′-bipyrene (**2**) in over 70 percent yield; the product was isolated according to the published procedure [59].

4.4. Treatment of Pyrene (1) With Periodic Acid (1:4 Mole Ratio)

A solution of pyrene (**1**), (2.02 g, 0.01 mole) in glacial acetic acid (50 ml) was stirred with an aqueous solution of periodic acid (9.2 g, 5 ml, 0.04 mole) at 50 °C for 2 min and then at 95 °C for 30 min; the grayish green **2** that originally crystallized out gradually changed to a brown-red solid. The product was filtered off, washed with glacial acetic acid (2×10 ml), and dried in a vacuum desiccator; yield 8.2–8.5 g, mp 245 to 250 °C (with evolution of iodine).

A sample washed with water, and dried to constant weight at room temperature, was analyzed. Found: C, 28.3; H, 1.23; I, 50.9.

A sample washed with glacial acetic acid, and dried at 25 °C/0.1 mm for 4 hr, was analyzed. Found: C, 18.6; H, 0.8; I, 59.0.

4.5. Oxidation of Naphthacene (3) to Naphthacenequinone (4)

A solution of naphthacene (**3**) (1.15 g, 0.005 mole) in *N*,*N*-dimethylformamide (100 ml) was stirred with an aqueous solution of periodic acid (4.6 g, 5 ml, 0.02 mole) at 120 °C for 8 min and then (to lessen the vigorous reaction) at 80 °C for 30 min. The reaction mixture was treated with water (50 ml), and cooled, to yield naphthacenequinone (**4**), 1.0–1.1g (80–85%), mp 278 to 281 °C. Sublimation at 200 °C/0.05 mm gave light-yellow needles, mp 288 to 290 °C, identical with an authentic sample [86, 87] by mixture mp, infrared spectrum, and thin-layer chromatography on silica gel G (250-μm layer, 5×20 cm glass plate) with 8:1:1 (v/v) benzene–*N*,*N*-dimethylformamide–acetic acid (solvent A), 60 min, R_f 0.70±0.02. On spraying with *ca.* 1.5*M* sulfuric acid in methanol (spray A) and heating (120 °C for 2 min), the yellow spot (thin-layer chromatogram), having a strong green fluorescence, changed to olive-brown.

4.6. Oxidation of Anthracene (5) to Anthraquinone (6)

A solution of anthracene (**5**) (3.56 g, 0.02 mole) in *N*,*N*-dimethylformamide (50 ml) was stirred with an aqueous solution of periodic acid (18.5 g, 40 ml, 0.08 mole) at 95 °C for 8 min, and then at 80 °C for 30 min. The rather dark reaction mixture was then cooled to about 5 °C; light-yellow needles of anthraquinone (**6**) crystallized out and were filtered off. The product was washed with methanol, and dried; yield 3.6–3.7 g (86–89%), mp 280 to 282 °C; dilution of the filtrate with water yielded an additional crop (0.2–0.3 g), bringing the total yield to 91–95 percent.

A sample purified by sublimation at 220 °C/0.05 mm, and recrystallized from glacial acetic acid, melted at 285 to 286 °C, lit [9] mp 281 to 282 °C: thin-layer chromatography on silica gel G (solvent A), 60 min, R_f 0.67±0.02. On a thin-layer chromatogram, quinone **6** gave a scarcely visible spot; spraying (spray A) and heating (120 °C) produced a strong yellow spot having a pink fluorescence.

4.7. Oxidation of Naphthalene (7) to 1,4-Naphthoquinone (9)

A solution of naphthalene (**7**) (2.56 g, 0.02 mole) in glacial acetic acid (75 ml) was stirred with an aqueous solution of periodic acid (18.5 g, 15 ml, 0.08 mole) at 110 °C for 8 min and then at 80 °C for 30 min. The reaction mixture was cooled, poured into about 250 ml of ice-cold water, and kept at room temperature for several hours. The yellow, powdery 1,4-naphthoquinone (**9**) was filtered off, washed with water, and dried; yield 2.0–2.3 g (67–72%). The product was purified by

column chromatography on silica gel with 2:1 (v/v) acetic acid–benzene as eluant to remove impurities (solvent A), R_f 0.90±0.01, R_f 0.83±0.01, R_f 0.54±0.02, and R_f 0.48±0.02 (probably due to 1,2-naphthoquinone). A sample recrystallized from ether and then from glacial acetic acid melted at 124 to 125 °C, lit [88] mp 125 °C; thin-layer chromatography on silica gel G (solvent A), 60 min, R_f 0.66±0.02. The yellow spot of **9** on a thin-layer chromatogram turns pink-brown on exposure to ultraviolet light.

4.8. Oxidation of Anthrone (8) to Anthraquinone (6)

A solution of anthrone [89] (**8**) (1.95 g, 0.02 mole) in glacial acetic acid (50 ml) was stirred with an aqueous solution of periodic acid (9.2 g, 5 ml, 0.04 mole) at 90 °C by the procedure described in section 4.6. The yield of anthraquinone (**6**) was 1.97 g (94%).

4.9. Oxidation of Phenanthrene (10) to Phenanthrenequinone (11)

A solution of phenanthrene (**10**) (3.56 g, 0.02 mole) in redistilled *p*-dioxane (50 ml) was stirred with an aqueous solution of periodic acid (18.6 g, 20 ml, 0.08 mole) at 95 °C for 5 to 7 min (or to the point where the clear, yellow solution just turned brown-red), and then at room temperature for 30 min. The reaction mixture was treated with water (20 ml), and stirred for 30 min in an ice-bath. The orange, crystalline product was filtered off, washed with 10 ml of 1:1 (v/v) cold, aqueous ethanol, and dried in the air. The thoroughly dry, orange product was stirred with cold benzene (20 ml), the suspension was filtered, and the solid was dried; yield of crude phenanthrenequinone (**11**) 1.6–1.8 g; concentration and cooling of the filtrate yielded an additional crop (0.3 g); total yield, 1.9–2.3 g (45–55%), mp 201 to 203 °C.

A sample recrystallized from benzene, and then from glacial acetic acid, melted at 205 to 207 °C, lit mp 205 °C [90], 198 °C [91]; thin-layer chromatography on silica gel G, (solvent A), 60 min, R_f 0.60±0.01. On spraying (spray A) and heating, the orange-yellow spot changed to olive-brown.

4.10. Oxidation of Benz[*a*]anthracene (12) to Benz[*a*]anthracene-7,12-dione (13)

A solution of benz[*a*]anthracene (**12**) (2.3 g, 0.01 mole) in *N*,*N*-dimethylformamide (40 ml) was stirred with an aqueous solution of periodic acid (9.2 g, 5 ml, 0.04 mole) at 100 °C for 10 min, and then at 85 °C for 30 min. The reaction mixture was then diluted with water (50 ml), and cooled in an ice-bath; yellow, powdery **13** was filtered off, washed with water, and dried; yield 1.9–2.9 g (70–78%). A good yield of the product was also obtained when acetic acid (50 ml, 110 °C) was used as the solvent.

The crude product was purified by column chromatography on silica gel with 1:1 (v/v) acetic acid–benzene to remove impurities (solvent A); R_f 0.53±0.02 and R_f 0.44±0.02 (strong green fluorescence). A sample recrystallized from methanol (charcoal), melted at 168 to 170 °C; lit mp 166 °C [92], 169 to 170 °C [93]; thin-layer chromatography on silica gel G (solvent A), 60 min, R_f 0.83±0.02. The yellow spot (pink fluorescence) of **13**, on spraying (spray A) and heating, darkened only very slowly.

4.11. Oxidation of Acenaphthene (15) to Acenaphthenequinone (16)

A solution of acenaphthene (**15**) (1.54 g, 0.01 mole) in glacial acetic acid (40 ml) was stirred with an aqueous solution of periodic acid (9.2 g, 6 ml, 0.04 mole) at 110 °C by the procedure described in section 4.6. Dilution with ice-water yielded a yellow, crystalline powder of **16**, 1.2–1.3 g (66–72%). The crude product was purified by column chromatography on silica gel with 3:1 (v/v) benzene–acetic acid. A sample recrystallized from glacial acetic acid gave yellow needles, mp 260 to 261 °C, lit mp 261 °C [94]; thin-layer chromatography on silica gel G, solvent A, 60 min, R_f 0.44±0.02.

4.12. Oxidation of Pentacene (17) to 6,13-Pentacenequinone (18)

A solution of pentacene (**17**) (0.28 g, 0.001 mole) in *N*,*N*-dimethylformamide (75 ml) was stirred with an aqueous solution of periodic acid (0.92 g, 2 ml, 0.004 mole) at 135 °C for 5 min, and then at 60 °C for 30 min. The reaction mixture was treated with water (35 ml), and cooled, to yield **18**, 0.250–0.267 g (81–87%), mp 382 to 384 °C. Sublimation at 250 °C/0.05 mm, followed by recrystallization from 1:1 (v/v) *N*,*N*-dimethylformamide–ethanol, gave light-yellow needles, mp 393 to 395 °C, lit mp 370 to 371 °C [95]; 394 °C [96]; thin-layer chromatography on silica gel G (solvent A), 60 min, R_f 0.78±0.01. The yellow spot (pink fluorescence), on spraying (spray A) and heating, turned cherry-red.

4.13. Oxidative Dimerization of Fluorene (20) to 1,2-Bis(2,2′-biphenylylene)ethylene (23)

A solution of fluorene (**20**) (1.66 g, 0.01 mole) in glacial acetic acid (50 ml) was stirred with an aqueous solution of periodic acid (5.7 g, 0.025 mole, 5 ml) at 110 °C for 15 min; the solution slowly turned orange-red, and a precipitate (iodic acid) appeared. The reaction mixture was treated with water (5 ml), stirred for an additional 15 min at 105 to 110 °C and then at room temperature (20 min), cooled (visible crystallization of the orange solid), and treated with an excess of cold water with stirring. The orange solid (sometimes mixed with a syrup) was separated by filtration (or decantation), dissolved in warm glacial acetic acid (50 ml), and passed through a column of silica gel (glacial acetic acid as eluant). Rechromatography of the orange band, and repeated recrystallization from warm glacial acetic acid, gave orange-red crystals of **23**, 0.16–0.18 g (9.6–10.8%) mp 185 to 187 °C, lit mp 182 to 183 °C [97]; 187 to 188 °C [98, 99]; thin-layer

chromatography on silica gel G with 4:3:3 (v/v) heptane–ethyl acetate–glacial acetic acid, 60 min, R_f 0.91 ± 0.01. When the reaction was conducted at 55 to 60 °C for 5 hr, the reaction mixture contained, in addition to compound **23**, a trace amount of fluoren-9-one; solvent A, 60 min, R_f 0.82 ± 0.01.

Hydrocarbon **23** belongs to the class of fulvalenes [100]; and alternative methods (and mechanisms) for preparation of **23** have recently been reviewed [100].

a. Attempted Oxidation of Biphenyl, Coronene, Fluoranthene, Perylene, *p*-Terphenyl, and Triphenylene

A solution of the hydrocarbon (0.001 to 0.01 mole) in acetic acid or 1:1 (v/v) acetic acid–*N*,*N*-dimethylformamide was stirred with aqueous periodic acid (0.004 to 0.04 mole) at 100 to 140° for 5 min, and then at 60 to 80° for 30 min. Treatment of the reaction mixture with water regenerated the starting compound, sometimes contaminated with iodine (thin-layer chromatography).

4.14 Oxidation of Pyrene (1), Anthracene (5), and Malonic Acid (14) in E.S.R. Cell

a. Pyrene (1)

An aliquot (0.4 ml) of pyrene (0.02 *M*, in glacial acetic acid) was pipeted into a cell and mixed with one drop of cold, aqueous periodic acid (0.5 *M*) at room temperature. The e.s.r. spectrum was immediately recorded, and showed the presence of free radicals.

b. Anthracene (5)

An aliquot (0.4 ml) of anthracene (0.2 *M*, in *N*,*N*-dimethylformamide) was cooled to about 0 °C, introduced into the cell, and mixed with two drops of cold, aqueous periodic acid (0.5 *M*); the e.s.r. spectrum was scanned from 0 to 60°, and showed no radicals. Another sample of anthracene (0.01 *M*, in acetic acid) was scanned from 20 to 60 °C, and showed no radicals; heating of the cell (boiling-water bath) and scanning of the spectrum did not reveal free radicals.

c. Malonic Acid (14)

An aliquot (0.4 ml) of malonic acid (0.3 *M*, in water) was mixed in the cell with two drops of aqueous periodic acid (0.5 *M*) at room temperature; the e.s.r. spectrum did not reveal any radicals; warming (hot-water bath) or cooling (ice-bath) of the cell and scanning of the spectrum did not reveal any radicals.

The oxidation was also repeated with aqueous sodium periodate solution; the result was negative.

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